



## PATENT ABSTRACTS OF JAPAN

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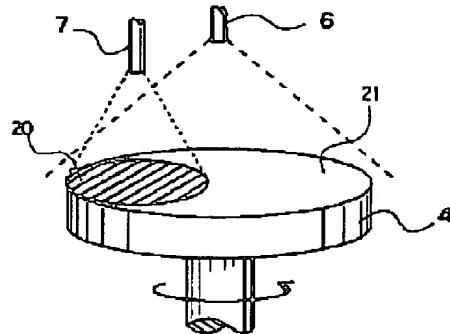
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FUJII AKIYUKI  
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TAKAYAMA RYOICHI(54) PRODUCTION OF OXIDE THIN FILM AND  
PRODUCTION DEVICE USED THEREFOR

(57) Abstract:

**PROBLEM TO BE SOLVED:** To form an oxide thin film excellent in characteristic on the surface of a large-area substrate uniformly at a high rate by supplying a reacting gaseous oxygen on the substrate surface in a pressure-reduced chamber and heating and rotating the substrate.

**SOLUTION:** A substrate holder 4 on which a substrate is mounted is rotated in an evacuated and pressure-reduced chamber and heated by a heater in the holder 4. Subsequently, a reacting gaseous oxygen is supplied on the entire surface of the substrate from a reacting gas supply means 6, and at least one kind of raw gas among  $\beta$ -diketone metal complex, metal alcoxide and cyclopentadienyl compd. is supplied on the film forming region 20 on the substrate surface from a raw gas supply means 7. The reacting gas is allowed to react with the raw gas on the region 20, the substrate is rotated to form an oxide thin film on an oxidizing and annealing region 21, and the thin film is annealed. The process is repeated, and a high-quality oxide thin film having excellent crystallinity, dielectric characteristic, piezoelectric characteristic electrical characteristic and insulating property is formed on the large area uniformly at a high rate.



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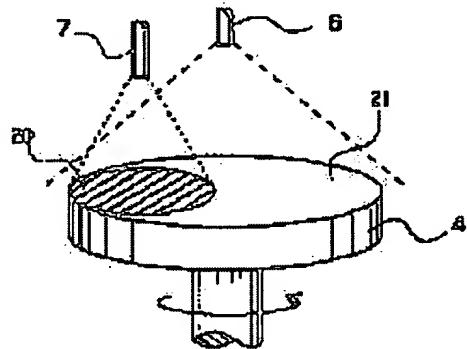
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## LEGAL STATUS

- [Date of request for examination]
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CLAIMS

## [Claim(s)]

[Claim 1] The manufacture method of the oxide thin film carried out [ being the manufacture method of the oxide thin film which forms an oxide thin film in the front face of the aforementioned substrate by supplying material gas and reactant gas to the front face of the substrate by which heating maintenance was carried out at predetermined temperature, supplying the aforementioned material gas only to the specific field in the supply field of the aforementioned reactant gas, and rotating the aforementioned substrate for the supply field of the aforementioned material gas in the supply field of the aforementioned reactant gas included partially, and ] as the feature.

[Claim 2] The manufacture method of an oxide thin film according to claim 1 that the aforementioned material gas is the steam of at least a kind of compound chosen from the group which consists of beta-diketone metal complex, a metal alkoxide, and a cyclopentadienyl compound.

[Claim 3] Oxide thin-film-fabrication equipment characterized by providing the following. The sealed reaction chamber. An exhaust air means to decompress the interior of the aforementioned reaction chamber. The substrate electrode holder for holding the substrate allotted in the aforementioned reaction chamber. A rotation means to rotate the aforementioned substrate electrode holder, the heating means for heating the aforementioned substrate, a reactant gas supply means to supply reactant gas to the front face of the aforementioned substrate, and a material gas supply means to supply material gas only to some fields of the front face of the aforementioned substrate.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

## [0001]

[The technical field to which invention belongs] this invention relates to the manufacture method of an oxide thin film used for various devices.

## [0002]

[Description of the Prior Art] The thin film of the oxide dielectric and piezo electric crystal represented by a perovskite type oxide, an ilmenite type oxide, the Ur Die Zeit type oxide, the bismuth stratified oxide, etc., the oxide magnetic compact represented by a spinel type oxide, a garnet type oxide, and the magnetoplumbite type oxide, and the oxide insulator represented by a NaCl type oxide and the corundum type oxide is considered in the application to many devices. The various manufacture methods, such as a vacuum deposition method, a spatter, the laser ablation method, the CVD (chemical vacuum deposition) method, the MOCVD (organic metalization study vacuum evaporation) method, and plasma CVD, are examined by formation of these thin films.

[0003] It is chemically stable, and the MOCVD method which was in the start raw material with beta-diketone metal complex, the metal alkoxide, or the cyclopentadienyl compound also in these does not have danger, such as toxicity and an ignition quality, and is safe. [ of (1) start raw material ]

(2) For a low reason, the decomposition temperature of a start raw material is possible for the crystal growth in low temperature.

(3) Film composition and membrane formation speed can control by the evaporation temperature and the carrier gas flow rate of a start raw material easily.

(4) In order that a reaction may occur gently on a substrate, there is no damage on a substrate or the front face of a crystal, and a good thin film is obtained.

(5) Equipment cost is cheap.

There is which feature and it excels in manufacture of an oxide thin film. This manufacture method supplies the oxygen which is material gas and reactant gas in the shape of a shower the whole surface on the substrate by which was held by the substrate electrode holder formed in the reaction chamber made reduced pressure, and heating maintenance was carried out at predetermined temperature (Fujimoto, spring water, Shiozaki, Fukagawa, the Nakatani monolithic-integrated-circuit technical symposium lecture collected works, 1992, p.120-125).

## [0004]

[Problem(s) to be Solved by the Invention] However, since beta-diketone metal complex, metal alkoxide, or cyclopentadienyl compound used for a start raw material also by the above-mentioned MOCVD method had low vapor pressure and it was difficult to supply material gas uniformly and in large quantities on a substrate at a large area, it was difficult to manufacture a quality oxide thin film uniformly and at high speed to a large area.

[0005] this invention solves these troubles in the conventional technology, and crystallinity aims a large area the oxide thin film excellent in many properties, such as dielectric characteristics, a piezo-electric property, magnetic properties, an electrical property, and an insulating property, at uniform and offering the manufacture method of the oxide thin film which can be manufactured at high speed highly

## [0006]

[Means for Solving the Problem] The manufacture method of the oxide thin film of this invention supplies alternatively the material gas which consists of steams, such as beta-diketone metal complex, a metal alkoxide, or a cyclopentadienyl compound, only to some fields of this front face, and carries out the chemical vacuum deposition of the oxide on a substrate by making it rotate, heating a substrate further while it supplies reactant gas to the front face of the substrate allotted in the reaction chamber which has an exhaust air means.

## [0007]

[Embodiments of the Invention] By supplying material gas and reactant gas to predetermined temperature on the front face of the substrate by which heating maintenance was carried out, the manufacture method of the oxide thin film of this invention is the manufacture method of the oxide thin film which forms an oxide thin film on the surface of a substrate, supplies material gas only to the specific field in the supply field of reactant gas, and is characterized by rotating a substrate for the supply field of material gas in the supply field of the reactant gas included partially. Thereby, in the field to which the material gas on the front face of a substrate is supplied, the thin film which consists of an oxide or other compounds is formed. the thin film formed when the substrate rotated and it moved out of this field — oxidization — and it anneals Thus, an oxide thin film is grown up with formation of a thin film, repeating oxidization and annealing by turns. At this time, it is desirable to make a substrate rotational frequency into 1 - 5000 revolution per minute. Moreover, it is desirable to set the degree of vacuum at the time of membrane formation to 0.1 - 500Torr.

[0008] The manufacture method of the oxide thin film of this invention can manufacture the thin film which consists of the following oxides at uniform and high speed to a large area.

1) An aluminum oxide, the corundum type oxide 2 represented by the oxide which makes a principal component Fe 2O3 and

them — BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, and Pb(Ti, Zr)O<sub>3</sub> and the perovskite type oxide 3 represented by the oxide which makes them a principal component — MgTiO<sub>3</sub> and LiNbO<sub>3</sub> — LiTaO<sub>3</sub> and them the ilmenite type represented by the oxide made into a principal component — the Ur Die Zeit type represented by the oxide which makes oxide 4ZnO and it a principal component — oxide 5BaBi2Nb 2O<sub>9</sub>, SrBi2Nb 2O<sub>9</sub>, SrBi2Ta 2O<sub>9</sub>, and SrBi2TaNb 2O<sub>9</sub> — Bismuth stratified oxide 6MgAl 2O<sub>4</sub>, Fe(nickel, Zn)2O<sub>4</sub> which are represented by the oxide which makes a principal component BaBi2Ta 2O<sub>9</sub>, SrBi4Ta 4O<sub>15</sub>, PbBi2Ta 2O<sub>9</sub>, PbBi2Nb 2O<sub>9</sub>, BaBi2TaNbO<sub>9</sub>, and them, (Mn, Zn) Fe 2O<sub>4</sub>, CoFe 2O<sub>3</sub>, and them Garnet type oxide 8BaFe 12O<sub>19</sub>, SrFe 12O<sub>19</sub>, PbFe 12O<sub>19</sub>, and them which are represented by the oxide which makes a principal component spinel mold oxide 7Y3Fe 5O<sub>12</sub>, Bi3Fe 5O<sub>12</sub>, and them which are represented by the oxide made into a principal component The NaCl type oxide represented by the oxide which makes a principal component magnetoplumbite mold oxide 9MgO, NiO, CoO, BaO, SrO and CdO, and them which are represented by the oxide made into a principal component [0009] The steam of at least a kind of compound chosen from the group which becomes material gas from beta-diketone metal complex, a metal alkoxide, and a cyclopentadienyl compound as a gestalt of desirable operation is used. When manufacturing which oxide thin film of a corundum type oxide, a perovskite type oxide, an ilmenite type oxide, the Ur Die Zeit type oxide, a bismuth stratified oxide, a spinel type oxide, a garnet type oxide, a magnetoplumbite type oxide, and a NaCl type oxide, it can manufacture at uniform and high speed to a large area by using for a start raw material beta-diketone metal complex, metal alkoxide, or cyclopentadienyl compound containing the metal which constitutes them. O<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>O, and O<sub>3</sub> can be used for reactant gas.

[0010] The oxide thin-film-fabrication equipment of this invention is equipped with the sealed reaction chamber, an exhaust air means to decompress the interior of a reaction chamber, the substrate electrode holder for holding the substrate allotted in the reaction chamber, a rotation means to rotate a substrate electrode holder, the heating means for heating a substrate, a reactant gas supply means to supply reactant gas to the front face of a substrate, and a material gas supply means to supply material gas only to some fields of the front face of a substrate.

[0011]

[Example] The manufacture method of the oxide thin film of one example of this invention is explained in detail using a drawing. The manufacturing installation of the oxide thin film used by this example is shown in drawing 1. In the reaction chamber 1, the substrate electrode holder 4 holding a substrate 3 is allotted, and it rotates at predetermined speed in the direction of the arrow in drawing by the rolling mechanism 8. The heater 2 for heating a substrate 3 is built in the substrate electrode holder 4. Moreover, the exhaust air means 5 for changing the interior of a reaction chamber 1 into a low voltage state is formed in the lower part of a reaction chamber 1. The material gas supply means 7 and the reactant gas supply means 6 are formed in the upper part of the substrate electrode holder 4. The carburetor 12 into which the start raw material 15 went through the bulb 11, and the further are connected with the carrier chemical cylinder 14 through the bulb 13 by the material gas supply means 7. Moreover, the reactant gas supply means 6 is connected with the reaction chemical cylinder 10 through the reactant gas supply bulb 9.

[0012] Hereafter, how to manufacture an oxide thin film using this manufacturing installation is explained. First, the inside of a reaction chamber 1 is exhausted by the exhaust air means 5, and the inside of a reaction chamber 1 is changed into a low voltage state. Subsequently, the material gas and reactant gas for forming the oxide thin film made into the purpose are supplied in a reaction chamber 1 from a carburetor 12 and the reaction chemical cylinder 10 by the material gas supply means 7 and the reactant gas supply means 6, respectively, heating a substrate 3 and rotating the substrate electrode holder 4 at a heater 2.

[0013] Drawing 2 is the perspective diagram (however, the substrate 3 is omitted) of the circumference of the substrate electrode holder 4. As shown in drawing 2, in the membrane formation field 20 which will contact material gas and reactant gas among the front faces of a substrate 3 if reactant gas is supplied from material gas and the reactant gas supply means 6, respectively, the pyrolysis of material gas and oxidation reaction advance on the front face of the heated substrate 3 from the material gas supply means 7, and a compound thin film is formed in it. Here, a substrate 3 is rotated, and when the formed compound thin film arrives at the oxidation annealing field 21 which does not contact material gas, it anneals a thin film while it oxidizes. If oxidation and the thin film which it annealed arrive at the membrane formation field 20 again, a thin film will be further formed on the thin film by which oxidation annealing processing was carried out. Thus, the quality oxide thin film which impurities, such as carbon it not only becomes possible to be able to form membranes uniformly to a large area, but contained in the start raw material when membranes are formed by the high rate of sedimentation, do not mix can be manufactured by repeating membrane formation, and oxidation and annealing.

[0014] Hereafter, how to manufacture the aluminum-oxide thin film of the corundum type crystal structure as an oxide thin film is explained concretely. Aluminium acetylacetonato (C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) aluminum 3 was used for the start raw material 15. The start raw material 15 was paid to the carburetor 12, and heating maintenance of this was carried out at 160 degrees C. To the substrate 3, these [ four ] were held with the substrate electrode holder 4 using the 6 inch silicon wafer, and heating maintenance was further carried out at the heater 2 at 850 degrees C.

[0015] First, the bulb 14 was opened and the argon which is carrier gas was supplied to the carburetor 12 by flow rate 1000sccm. Subsequently, the bulb 11 was opened and the steam of aluminium acetylacetonato was supplied in the reaction chamber 1 by the material gas supply means 7 with argon gas. Furthermore the bulb 9 was opened and the oxygen as reactant gas was supplied in the reaction chamber 1 by the reactant gas supply means 6 by flow rate 800sccm. Thus, it was made to react for 30 minutes and the aluminum-oxide thin film was formed on the substrate 3. In addition, the rotational frequency of the substrate 3 at this time was made into 400 revolutions per minute, and the degree of vacuum at the time of membrane formation was set to 5Torr(s). Then, the substrate 3 was cooled to near a room temperature, and it took out from the reaction chamber 1.

[0016] As a result of an X diffraction's investigating the crystal structure of the obtained thin film, the corundum type crystal structure was carried out. The obtained thin film was observed with the scanning electron microscope (SEM). Consequently, thickness was 4 micrometers and the particle size of a microcrystal was 0.2 micrometers. Neither film peeling nor the crack was seen. In addition, the thickness distribution of the formed thin film was less than 2% also in any of four substrates 3, and dispersion in film composition was also less than 3%. Moreover, film composition was investigated by the Auger electron spectral-analysis (AES) method. Consequently, the peak by impurities other than aluminum and O was not seen.

[0017]

[Effect of the Invention] Since membranes can be formed according to this invention, repeating formation of an oxide thin film,

oxidization of this thin film, and annealing by turns on a substrate, a quality oxide thin film can be manufactured uniformly and at high speed to a large area.

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DESCRIPTION OF DRAWINGS

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## [Brief Description of the Drawings]

[Drawing 1] It is the cross section of the oxide thin-film-fabrication equipment used for the example of this invention.

[Drawing 2] It is the perspective diagram of the circumference of the substrate electrode holder of this manufacturing installation.

## [Description of Notations]

- 1 Reaction Chamber
- 2 Heater
- 3 Substrate
- 4 Substrate Electrode Holder
- 5 Exhaust Air Means
- 6 Reactant Gas Supply Means
- 7 Material Gas Supply Means
- 8 Rolling Mechanism
- 9 Bulb
- 10 Reaction Chemical Cylinder
- 11 Bulb
- 12 Carburetor
- 13 Bulb
- 14 Carrier Chemical Cylinder
- 15 Start Raw Material
- 20 Membrane Formation Field
- 21 Oxidization Annealing Field

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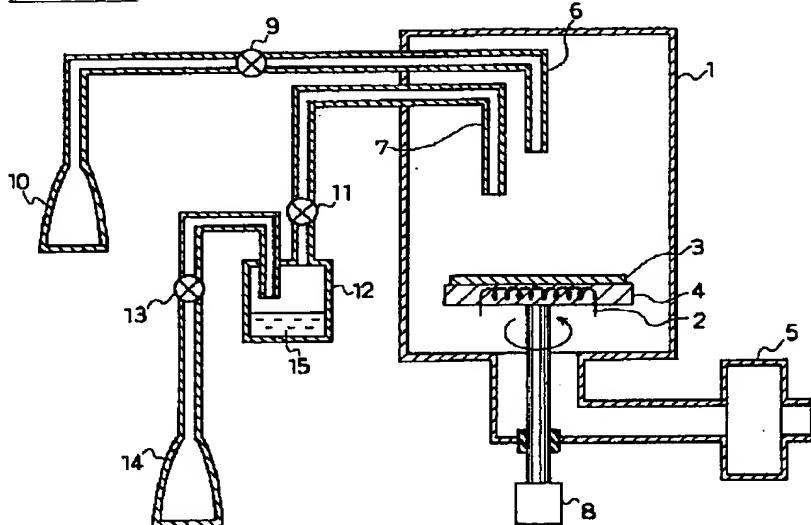
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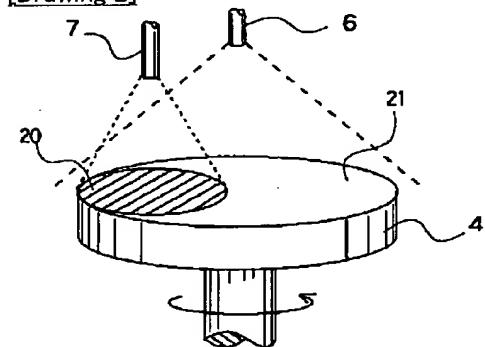
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## DRAWINGS

## [Drawing 1]



## [Drawing 2]



4 基板ホルダ  
6 反応ガス供給手段  
7 原料ガス供給手段

20 成膜領域  
21 酸化アニール領域

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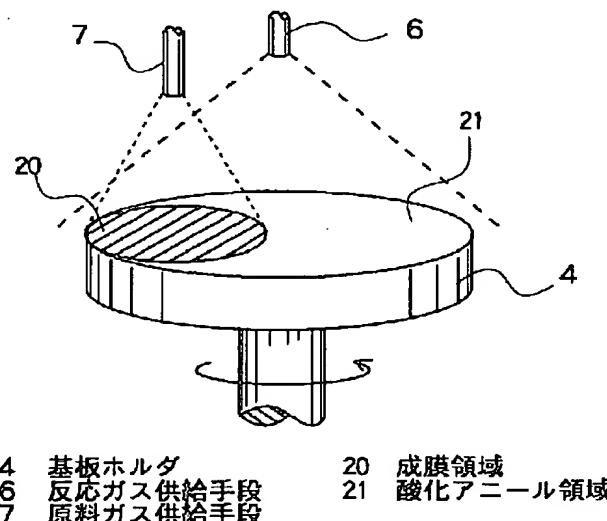
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(54)【発明の名称】 酸化物薄膜の製造方法およびそれに用いる製造装置

(57)【要約】

【課題】 均一な酸化物薄膜を大面積かつ高速で製造する。

【解決手段】 所定温度に加熱保持された基板の表面に原料ガスおよび反応ガスを供給することにより基板の表面に酸化物薄膜を形成する酸化物薄膜の製造方法であって、原料ガスを反応ガスの供給領域内の特定の領域のみに供給し、基板を原料ガスの供給領域を部分的に含む反応ガスの供給領域で回転させることにより、基板上で薄膜の形成と薄膜の酸化およびアニールを交互に繰り返しながら酸化物薄膜を成長させる。



## 【特許請求の範囲】

【請求項1】 所定温度に加熱保持された基板の表面に原料ガスおよび反応ガスを供給することにより前記基板の表面に酸化物薄膜を形成する酸化物薄膜の製造方法であって、前記原料ガスを前記反応ガスの供給領域内の特定の領域のみに供給し、前記基板を前記原料ガスの供給領域を部分的に含む前記反応ガスの供給領域で回転させることを特徴とする酸化物薄膜の製造方法。

【請求項2】 前記原料ガスが、 $\beta$ -ジケトン金属錯体、金属アルコキシドおよびシクロペニタジエニル化合物からなる群より選択される少なくとも一種の化合物の蒸気である請求項1記載の酸化物薄膜の製造方法。

【請求項3】 密閉された反応チャンバと、前記反応チャンバの内部を減圧する排気手段と、前記反応チャンバ内に配された基板を保持するための基板ホルダと、前記基板ホルダを回転させる回転手段と、前記基板を加熱するための加熱手段と、前記基板の表面に反応ガスを供給する反応ガス供給手段と、前記基板の表面の一部の領域のみに原料ガスを供給する原料ガス供給手段を備えた酸化物薄膜製造装置。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、種々のデバイスに用いられる酸化物薄膜の製造方法に関するものである。

## 【0002】

【従来の技術】 ペロブスカイト型酸化物、イルメナイト型酸化物、ウルツァイト型酸化物およびビスマス層状酸化物などに代表される酸化物誘電体・圧電体や、スピネル型酸化物、ガーネット型酸化物およびマグネットラムバイト型酸化物に代表される酸化物磁性体や、 $\text{NaCl}$ 型酸化物およびコランダム型酸化物に代表される酸化物絶縁体の薄膜は、多くのデバイスへの応用が考えられている。これらの薄膜の形成には、真空蒸着法、スパッタ法、レーザアブレーション法、CVD（化学蒸着）法、MOCVD（有機金属化学蒸着）法、プラズマCVDなど様々な製造方法が検討されている。

【0003】 これらのなかでも出発原料に $\beta$ -ジケトン金属錯体、金属アルコキシドまたはシクロペニタジエニル化合物をもちいたMOCVD法は、

(1) 出発原料が化学的に安定で、毒性や発火性などの危険性が無く、安全である。

(2) 出発原料の分解温度が低いため低温での結晶成長が可能である。

(3) 膜組成および成膜速度が出発原料の気化温度やキャリアガス流量により容易に制御できる。

(4) 基板上で緩やかに反応が起きるため、基板や結晶表面のダメージがなく、良質の薄膜が得られる。

(5) 装置コストが安い。  
などの特長があり、酸化物薄膜の製造に優れている。この製造方法は、減圧にした反応チャンバー内に設けた基

板ホルダによって保持されかつ所定温度に加熱保持された基板上の全面に、原料ガスおよび反応ガスである酸素をシャワー状に供給するようにしたものである（藤本、清水、塩崎、深川、中谷：半導体・集積回路技術シンポジウム講演論文集、1992、p. 120～125）。

## 【0004】

【発明が解決しようとする課題】 しかしながら、上記のMOCVD法によっても、出発原料に用いる $\beta$ -ジケトン金属錯体、金属アルコキシドまたはシクロペニタジエニル化合物は、蒸気圧が低く、基板上に大面積に均一にかつ大量に原料ガスを供給することが難しいため、高品質の酸化物薄膜を大面積に均一かつ高速に製造することは困難であった。

【0005】 本発明は、従来技術におけるこれらの問題点を解決し、結晶性が高く、誘電特性、圧電特性、磁気特性、電気特性、絶縁特性等の諸特性に優れた酸化物薄膜を大面積に均一かつ高速で製造することができる酸化物薄膜の製造方法を提供することを目的とする。

## 【0006】

【課題を解決するための手段】 本発明の酸化物薄膜の製造方法は、排気手段を有する反応チャンバ内に配された基板の表面に反応ガスを供給するとともに、同表面の一部の領域のみに $\beta$ -ジケトン金属錯体または金属アルコキシドまたはシクロペニタジエニル化合物等の蒸気からなる原料ガスを選択的に供給し、さらに基板を加熱しながら回転させることによって基板上に酸化物を化学蒸着するものである。

## 【0007】

【発明の実施の形態】 本発明の酸化物薄膜の製造方法は、所定温度に加熱保持された基板の表面に原料ガスおよび反応ガスを供給することにより基板の表面に酸化物薄膜を形成する酸化物薄膜の製造方法であって、原料ガスを反応ガスの供給領域内の特定の領域のみに供給し、基板を原料ガスの供給領域を部分的に含む反応ガスの供給領域で回転させることを特徴とするものである。これにより、基板表面の原料ガスの供給される領域では酸化物あるいはその他の化合物からなる薄膜が形成される。基板が回転し、同領域外に移動すると、形成された薄膜は、酸化およびアニールされる。このように、薄膜の形成と、酸化・アニールを交互に繰り返しながら酸化物薄膜を成長させるものである。このとき、基板回転数を1～500回転/分とすることが好ましい。また、成膜時の真空度を0.1～500 Torrとすることが好ましい。

【0008】 本発明の酸化物薄膜の製造方法は、以下の酸化物からなる薄膜を大面積に均一かつ高速で製造することができる。

- 1) 酸化アルミニウム、 $\text{Fe}_2\text{O}_3$ およびそれらを主成分とする酸化物に代表されるコランダム型酸化物
- 2)  $\text{BaTiO}_3$ 、 $\text{SrTiO}_3$ 、 $\text{Pb}(\text{Ti}, \text{Zr})\text{O}$

、およびそれらを主成分とする酸化物に代表されるペロブスカイト型酸化物

3)  $MgTiO_3$ 、 $LiNbO_3$ 、 $LiTaO_3$ およびそれらを主成分とする酸化物に代表されるイルメナイト型酸化物

4)  $ZnO$ およびそれを主成分とする酸化物に代表されるウルツタイト型酸化物

5)  $BaBi_2Nb_2O_9$ 、 $SrBi_2Nb_2O_9$ 、 $SrBi_2Ta_2O_9$ 、 $SrBi_2TaNb_2O_9$ 、 $BaBi_2Ta_2O_9$ 、 $SrBi_4Ta_4O_{15}$ 、 $PbBi_2Ta_2O_9$ 、 $PbBi_2Nb_2O_9$ 、 $BaBi_2TaNbO_9$ およびそれらを主成分とする酸化物に代表されるビスマス層状酸化物

6)  $MgAl_2O_4$ 、 $(Ni, Zn)Fe_2O_4$ 、 $(Mn, Zn)Fe_2O_4$ 、 $CoFe_2O_4$ およびそれらを主成分とする酸化物に代表されるスピネル型酸化物

7)  $Y_3Fe_5O_{12}$ 、 $Bi_3Fe_5O_{12}$ およびそれらを主成分とする酸化物に代表されるガーネット型酸化物

8)  $BaFe_{12}O_{19}$ 、 $SrFe_{12}O_{19}$ 、 $PbFe_{12}O_{19}$ およびそれらを主成分とする酸化物に代表されるマグネットラムバイト型酸化物

9)  $MgO$ 、 $NiO$ 、 $CoO$ 、 $BaO$ 、 $SrO$ 、 $CdO$ およびそれらを主成分とする酸化物に代表される $NaC_1$ 型酸化物

【0009】好ましい実施の形態としては、原料ガスに、 $\beta$ -ジケトン金属錯体、金属アルコキシドおよびシクロペンタジエニル化合物からなる群より選択される少なくとも一種の化合物の蒸気を用いるものである。コランダム型酸化物、ペロブスカイト型酸化物、イルメナイト型酸化物、ウルツタイト型酸化物、ビスマス層状酸化物、スピネル型酸化物、ガーネット型酸化物、マグネットラムバイト型酸化物および $NaC_1$ 型酸化物のいずれの酸化物薄膜を製造する場合においても、それらを構成する金属を含む $\beta$ -ジケトン金属錯体、金属アルコキシドまたはシクロペンタジエニル化合物を出発原料に用いることにより、大面積に均一かつ高速で製造することができる。反応ガスには、 $O_2$ 、 $N_2O$ 、 $H_2O$ および $O_3$ を用いることができる。

【0010】本発明の酸化物薄膜製造装置は、密閉された反応チャンバと、反応チャンバの内部を減圧する排気手段と、反応チャンバ内に配された基板を保持するための基板ホルダと、基板ホルダを回転させる回転手段と、基板を加熱するための加熱手段と、基板の表面に反応ガスを供給する反応ガス供給手段と、基板の表面の一部の領域のみに原料ガスを供給する原料ガス供給手段を備えたものである。

【0011】

【実施例】本発明の一実施例の酸化物薄膜の製造方法を図面を用いて詳細に説明する。本実施例で用いた酸化物薄膜の製造装置を図1に示す。反応チャンバ1内には、基板3を保持する基板ホルダ4が配されており、回転機

構8により図中矢印方向に所定速度で回転する。基板ホルダ4には基板3を加熱するためのヒータ2が内蔵されている。また、反応チャンバ1の下部には、反応チャンバ1の内部を低圧状態にするための排気手段5が設けられている。基板ホルダ4の上部には、原料ガス供給手段7および反応ガス供給手段6が設けられている。原料ガス供給手段7は、バルブ11を通じて出発原料15の入った気化器12、さらにはバルブ13を通じてキャリアガスボンベ14とつながっている。また、反応ガス供給手段6は、反応ガス供給バルブ9を通じて反応ガスボンベ10とつながっている。

【0012】以下、本製造装置を用いて酸化物薄膜を製造する方法について説明する。まず、反応チャンバ1内を排気手段5によって排気し、反応チャンバ1内を低圧状態にする。次いで、ヒータ2によって基板3を加熱し、基板ホルダ4を回転させながら、目的とする酸化物薄膜を形成するための原料ガスおよび反応ガスを、それぞれ気化器12および反応ガスボンベ10より、原料ガス供給手段7および反応ガス供給手段6によって反応チャンバ1内に供給する。

【0013】図2は、基板ホルダ4周りの斜視図（ただし基板3は省略している）である。図2に示すように、加熱した基板3の表面に、原料ガス供給手段7から原料ガス、反応ガス供給手段6から反応ガスをそれぞれ供給すると、基板3の表面のうち、原料ガスおよび反応ガスと接触する成膜領域20において原料ガスの熱分解と酸化反応が進行し、化合物薄膜が形成される。ここで、基板3を回転させ、形成された化合物薄膜が原料ガスと接触しない酸化アニール領域21に達すると、薄膜は酸化されるとともにアニールされる。酸化およびアニールされた薄膜が再び成膜領域20に達すると、酸化アニール処理された薄膜の上にさらに薄膜が形成される。このようにして、成膜と、酸化、アニールを繰り返すことにより、大面積に均一に成膜できることが可能となるばかりでなく、高堆積速度で成膜した場合においても、出発原料に含まれているカーボンなどの不純物が混入しない高品質の酸化物薄膜を製造することができる。

【0014】以下、酸化物薄膜としてコランダム型結晶構造の酸化アルミニウム薄膜を製造する方法について具体的に説明する。出発原料15にはアルミニウムアセチルアセトナートA1 ( $C_5H_7O_2$ )<sub>3</sub>を用いた。気化器12に出発原料15を入れ、これを160℃に加熱保持した。基板3には6インチシリコンウエハを4枚用い、これらを基板ホルダ4により保持し、さらにヒータ2により850℃に加熱保持した。

【0015】まず、バルブ14を開き、キャリアガスであるアルゴンを流量1000sccmで気化器12に供給した。次いで、バルブ11を開き、アルミニウムアセチルアセトナートの蒸気を、アルゴンガスとともに原料ガス供給手段7により反応チャンバ1内に供給した。さ

らにバルブ9を開き、反応ガスとしての酸素を流量800 sccmで反応ガス供給手段6により反応チャンバ1内に供給した。このようにして30分間反応させ、基板3上に酸化アルミニウム薄膜を形成した。なお、このときの基板3の回転数は400回転/分とし、成膜時の真空度は5 Torrとした。その後、基板3を室温付近まで冷却し、反応チャンバ1から取り出した。

【0016】得られた薄膜の結晶構造をX線回折により調べた結果、コランダム型の結晶構造をしていた。得られた薄膜を走査型電子顕微鏡(SEM)で観察した。その結果、膜厚は4 μmで、結晶子の粒径は0.2 μmであった。膜はがれやクラックは見られなかった。なお、形成された薄膜の膜厚分布は、4枚の基板3のいずれにおいても2%以内であり、膜組成のばらつきも3%以内であった。また、オージェ電子分光分析(AES)法により膜組成を調べた。その結果、AlとO以外の不純物によるピークは見られなかった。

#### 【0017】

【発明の効果】本発明によれば、基板上にて酸化物薄膜の形成と同薄膜の酸化およびアニールとを交互に繰り返しながら成膜することができるため、高品質の酸化物薄膜を大面積に均一かつ高速に製造することができる。

#### 【図面の簡単な説明】

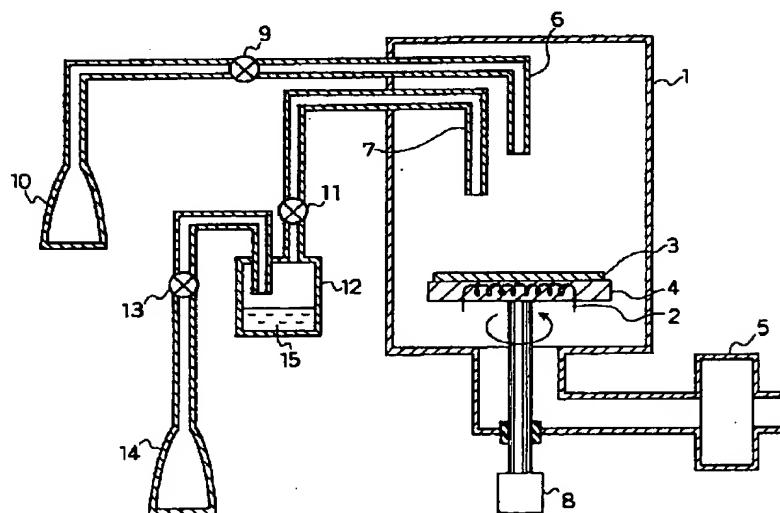
【図1】本発明の実施例に用いた酸化物薄膜製造装置の断面図である。

【図2】同製造装置の基板ホルダ周囲の斜視図である。

#### 【符号の説明】

- 1 反応チャンバ
- 2 ヒータ
- 3 基板
- 4 基板ホルダ
- 5 排気手段
- 6 反応ガス供給手段
- 7 原料ガス供給手段
- 8 回転機構
- 9 バルブ
- 10 反応ガスボンベ
- 11 バルブ
- 12 気化器
- 13 バルブ
- 14 キャリアガスボンベ
- 15 出発原料
- 20 成膜領域
- 21 酸化アニール領域

【図1】



【図2】

